

# Thermodynamics of carrier-mediated magnetism in semiconductors

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We propose a model of carrier-mediated ferromagnetism in semiconductors that accounts for the temperature dependence of the carriers. The model permits analysis of the thermodynamic stability of competing magnetic states, opening the door to the construction of magnetic phase diagrams. As an example we analyze the stability of a possible *reentrant* ferromagnetic semiconductor, in which increasing temperature leads to an increased carrier density, such that the enhanced exchange coupling between magnetic impurities results in the onset of ferromagnetism as temperature is raised.

Ferromagnetic semiconductors (FS) show important and potentially useful differences from their metallic counterparts. For example, if the magnetism in a magnetically doped semiconductor is mediated by carriers, then changes in the carrier density induced by light or applied bias may significantly alter the exchange interaction between the carriers and magnetic impurities. When this effect is sufficient to turn the ferromagnetism on or off, there arise intriguing possibilities for light- or bias-controlled ferromagnetism [1, 2, 3, 4] not possible in conventional ferromagnetic metals.

Another approach to controlling ferromagnetism in FS materials is to exploit the strong temperature dependence of carrier density that is the hallmark of semiconductors. Despite this dependence, most theoretical analysis of FS has assumed a metallic-like picture [5, 6] in which carrier density is treated as independent of temperature. Consequently, a number of experimental features observed in certain FS materials remain incompletely explained. Examples include the metal-insulator transition [7] in Mn-doped GaAs; the role of the impurity band in oxide FS materials [8, 9]; and the resistivity peak in Mn-doped GaAs observed near the Curie temperature,  $T_C$ , which is usually attributed to temperature-dependent scattering [10] just as in metals [11]. In each of these cases, correct treatment of the temperature dependence of the carrier density could substantively change our understanding of the observed phenomena.

In this paper we develop a theoretical model of ferromagnetism in semiconductors that includes the temperature dependence of the carriers. By providing a way to analyze the thermodynamic stability of different competing magnetic states, this model makes possible the self-consistent calculation of the magnetic phase diagram of a FS. Here we use the model to calculate the temperature-dependent magnetization of a simple generic FS. In contrast to the standard monotonic decay of the magnetization with increasing temperature found in metals, we demonstrate the possibility of stable “reentrant” ferromagnetism in semiconductors: as the temperature is increased the resulting higher density of thermally excited carriers can enhance the exchange coupling between mag-

netic impurities—and thereby *increase* the magnetization over some range of temperatures. Of course, whether such a possibility can be realized even in principle depends on the thermodynamic stability of the reentrant phase relative to other magnetic states. To properly analyze this competition requires a theoretical framework for computing the free energy of each possible magnetic state. Our model provides this framework.

We begin by considering a FS doped with donors of density  $N_d$  and with magnetic impurities of density  $N_i$ . For simplicity we assume that no acceptors are present, that electrons are the only carriers, and that the magnetic impurities are electrically neutral; the more general case is straightforward. The interaction between electron spins  $\vec{s}_i$  and localized impurity spins  $\vec{J}_j$  is taken to be

$$H_{ex} = -\Gamma_{ex} \sum_{i,j} \delta(\vec{r}_i - \vec{R}_j) \vec{s}_i \cdot \vec{J}_j, \quad (1)$$

where  $\Gamma_{ex}$  is the exchange coupling and  $\vec{r}_i$  ( $\vec{R}_j$ ) is the position of the carrier (impurity). We assume a nondegenerate semiconductor in which the conduction band is separated from the donor level (or impurity band) by  $\varepsilon_d$  in the absence of magnetic order, as in Fig. 1(a). When magnetic order is present the conduction band and donor level experience spin splittings of  $\Delta$  [12] and  $\Delta_d$  [13], respectively, as in Fig. 1(b). For simplicity we assume that the ratio  $\Delta_d/\Delta \equiv \gamma$  has a fixed, material-specific value.

These spin splittings can arise from either an applied magnetic field or from the carrier-impurity interaction, and in general will modify the temperature-dependence of the electron density [14]. We can obtain an expression for the density  $n$  of conduction electrons as follows. Electroneutrality requires that  $n + N_d^0 = N_d$ , where  $N_d^0$  is the density of neutral (non-ionized) donors. If we take the effective density of states in the conduction band as  $N_c = (1/4)(2m^*k_B T/\pi\hbar^2)^{3/2}$  [15], then the electroneutrality condition can be satisfied by introducing the chemical potential  $\mu$  that satisfies  $N_c \exp(\mu/k_B T) \cosh(\Delta/2k_B T) = N_d/[1 + 2 \exp[(\mu + \varepsilon_d)/k_B T] \cosh(\Delta_d/2k_B T)]$ . This is equivalent to a quadratic equation in the electron den-

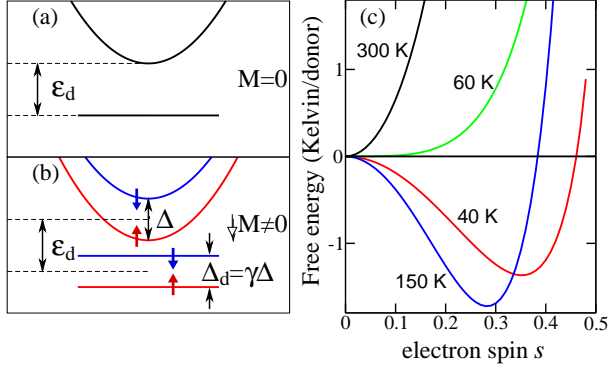


FIG. 1: Schematic energy-band structure, and temperature evolution of free energy. (a) In the absence of magnetization ( $M = 0$ ) both the conduction band and the donor level (at  $-\varepsilon_d$  relative to the band edge) are unsplit. (b) The onset of magnetic order ( $M \neq 0$ ) leads to spin splitting  $\Delta$  of the conduction band and  $\Delta_d$  of the donor level. Thick arrows represent two spin projections. (c) Free energy  $\mathcal{F}$  versus average electron spin  $s$ . Materials parameters were chosen based on Gd-doped EuO [21]:  $\Gamma_{ex} = 40 \text{ eV} \cdot \text{\AA}^3$ ,  $|\varepsilon_d| = 20 \text{ meV}$ ,  $N_d = 3.5 \times 10^{19} \text{ cm}^{-3}$ ,  $m^* = 2$ , lattice constant  $a_0 = 5.15 \text{ \AA}$ ,  $N_i = 4/a_0^3$ ,  $\gamma = 1$ ,  $a_B = 8 \text{ \AA}$ , and  $J = 7/2$ . Behavior at 40 and 150 K reveals ferromagnetic states.

sity, and has the solution

$$n(s, T) = \frac{1}{2} N_d \kappa(s, T) \left[ \sqrt{1 + 4/\kappa(s, T)} - 1 \right]. \quad (2)$$

Here we have expressed the dependence of  $n$  on the splitting  $\Delta$  equivalently as a dependence on the average spin of the conduction electrons,  $s = (1/2) \tanh(\Delta/2k_B T)$ . We have also defined the auxiliary function  $\kappa(s, T) = (N_c/N_d) \exp(-\varepsilon_d/k_B T) (1 - 4s^2)^{(\gamma-1)/2} / [(1+2s)^\gamma + (1-2s)^\gamma]$ . In addition, for later use it is here convenient to introduce the *relative* density of conduction electrons  $\nu(s, T) = n(s, T)/N_d$ , so that  $0 < \nu(s, T) < 1$ .

In the magnetically ordered state, both the conduction electrons and the electrons bound to donors experience the field from the ordered impurity spins. The impurity spins in turn experience both a long-ranged uniform field from the delocalized conduction electrons and a short-ranged field from the bound donor electrons. This situation can be described using two coupled order parameters: the average spin  $s$  of the conduction electrons as defined above; and the average spin  $m = M/N_i g_i \mu_B$  of the impurities (here  $M$  is the total magnetization due to the impurities and  $g_i$  is the electron  $g$ -factor).

Using these two order parameters, we can write the free-energy density of the system in the form

$$\mathcal{F} = \mathcal{F}_i + \mathcal{F}_e - \Gamma_{ex} N_i N_d [\nu(s, T) s + \nu_d(s, T) s_d] m. \quad (3)$$

Here  $\mathcal{F}_i = \mathcal{F}_i(m)$  is the contribution from the entropy of the impurity spins, and  $\mathcal{F}_e = \mathcal{F}_e(s)$  is the contribution from the entropy of the conduction electrons. The former can be obtained by expressing the free energy of the

impurity spins as a function of an external magnetic field and then applying a Legendre transformation [16]. This gives

$$\mathcal{F}_i(m) = N_i k_B T \left[ 2J\alpha(m) - \ln \frac{\sinh[(2J+1)\alpha(m)]}{\sinh[\alpha(m)]} \right], \quad (4)$$

where  $\alpha(m) = B_J^{-1}(m/J)/2J$ , and  $B_J^{-1}(x)$  denotes the inverse of the Brillouin function [15].

The electron contribution  $\mathcal{F}_e(s)$  can be derived using a similar approach. We first define the density-weighted average spin of conduction and donor electrons,

$$\tau(s, T) = \nu(s, T) s + [1 - \nu(s, T)] s_d, \quad (5)$$

where the average spin of donor electrons is given by  $s_d = (1/2)[(1+2s)^\gamma - (1-2s)^\gamma]/[(1+2s)^\gamma + (1-2s)^\gamma]$ . We next invert the function  $\tau(s, T)$  by solving Eq. (5) for  $s = s(\tau, T)$ . This function can then be used to obtain the free energy of the conduction and donor electrons:

$$\mathcal{F}_e(s) = k_B T N_d \int_0^{\tau(s, T)} \ln \frac{1 + 2s(\tau', T)}{1 - 2s(\tau', T)} d\tau'. \quad (6)$$

The third term in Eq. (3) is the mean-field approximation for the internal energy described by the exchange Hamiltonian of Eq. (1). This term represents the coupling of the order parameters  $s$  and  $m$ . The expression in square brackets makes explicit the separate contributions from conduction electrons and donor electrons. Since the conduction electrons are delocalized, they mediate a long-ranged interaction between impurity spins. In contrast, the interaction between donor electrons and impurity spins is short-ranged, and is controlled by a contact term given by the value of the donor wavefunction at the impurity site. We turn now to evaluating this interaction by deriving an explicit expression for the term  $\nu_d(s, T)$  appearing in Eq. (3).

We use a “two-color” percolation model to represent the short-ranged interaction between the randomly distributed donor electrons and impurity spins [17, 18]. This model is a generalization of a more standard percolation approach originally proposed for dilute ferromagnets [19] and recently applied to magnetic semiconductors [20]. Within the two-color model, an interaction is counted for each pair of sites whose spatial separation is less than  $R_c = [B_c/(4\pi/3)]^{1/3} (N_i N_d^0)^{-1/6}$ , where  $B_c \approx 2.7$  is the average coordination number [17]. The density of such pairs within the infinite percolation network is  $N_{cl} B_c/2$ , where  $N_{cl} = 2/(4\pi R_c/3)^3$  is the average density of donor- and impurity-sites belonging to the network.

Within the mean-field approximation, the contribution of these pairs to the internal energy can be shown to be  $U_{cl} = -\Gamma_{ex} |\psi(0)|^2 \exp(-2R_c/a_B) (1/2) N_{cl} B_c m s_d$ , where  $\psi(0)$  is the value of the donor wavefunction at the origin ( $|\psi(0)|^2 = 1/\pi a_B^3$  for hydrogenic donors). Comparing this result to Eq. (3) implies that

$$\nu_d = |\psi(0)|^2 (N_i N_d)^{-1/2} (1 - \nu)^{1/2} \exp(-2R_c/a_B). \quad (7)$$

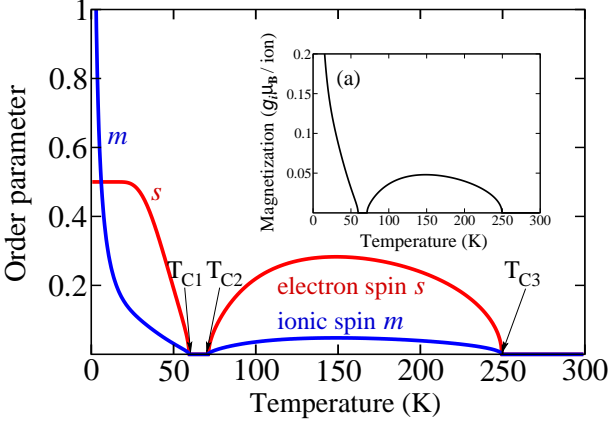


FIG. 2: Temperature dependence of order parameters  $s$  and  $m$ , showing reentrant behavior at  $T = T_{C2}$  as temperature is raised. Curie temperatures  $T_{C1,2,3}$ , at which  $m$  and  $s$  both vanish, define phase boundaries between two ferromagnetic and two paramagnetic states. (a) Inset: Temperature dependence of the combined average spin from all electrons. Materials parameters are the same as in Fig. 1.

Having now obtained explicit expressions for all the terms in Eq. (3), we can directly obtain the temperature dependence of the order parameters  $s$  and  $m$  by minimizing the free energy  $\mathcal{F}$ . This results in

$$s = \frac{1}{2} \tanh \left[ \frac{\Gamma_{ex} N_i m}{2k_B T} \frac{\partial [\tilde{\nu}(s, T) s]}{\partial \tau(s, T)} \right], \quad (8)$$

$$m = JB_J \left[ \frac{J \Gamma_{ex} N_d \tilde{\nu}(s, T) s}{k_B T} \right], \quad (9)$$

where  $\tilde{\nu}(s, T) = \nu(s, T) + \nu_d(s, T) s_d/s$ . By expanding Eqs. (8) and (9) for small  $s$  and  $m$  we obtain an implicit expression for the critical temperature:

$$T_C = T_C^0 \tilde{\nu}(0, T_C) / [\gamma + (1 - \gamma) \nu(0, T_C)]^{1/2}, \quad (10)$$

where  $T_C^0 = (\Gamma_{ex}/k_B)[N_i N_d J(J+1)/12]^{1/2}$  is the Curie temperature in the limit of completely ionized donors [9].

We now turn to exploring the predictions of our model for a realistic example. We choose materials parameters approximately corresponding to Gd-doped EuO [21], a magnetic material known to exhibit strong temperature dependence of the carrier density. Fig. 1(c) shows the resulting free energy  $\mathcal{F}$  as a function of conduction-electron spin  $s$ , at the temperatures 40, 60, 150, and 300 K. A ferromagnetic state (at 150 K) appears at *higher* temperature than a paramagnetic state (at 60 K), and is thus a reentrant ferromagnetic state. This phenomenon is a direct consequence of the increased number of thermally excited carriers, which sufficiently increase the exchange coupling between magnetic impurities to overcome the additional entropic cost of a magnetically ordered state.

Figure 2 shows the temperature dependence of  $s(T)$  and  $m(T)$  for the same materials parameters. For this example there are three different solutions of Eq. (10) for  $T_C$ , as shown. The reentrant ferromagnetic state exists in the temperature range  $T_{C1} \leq T \leq T_{C2}$ . The inset shows the temperature dependence of the combined average spin from all electrons (conduction, donor, and impurity), revealing behavior very different from the conventional monotonic decay [15].

In the standard theoretical description of dilute magnetic semiconductors the ferromagnetism is mediated entirely by “free” carriers (usually holes in the valence band) [5, 6]. An important check of our theory is that it reproduces earlier results obtained in this limit. We thus consider the case with all donors ionized,  $n = N_d$ . In this regime the entropy contribution  $\mathcal{F}_e(s)$  must be replaced with its degenerate counterpart for the internal energy,  $\mathcal{F}_e^{\text{deg}}(s) = (3nE_F/10) [(1+2s)^{5/3} + (1-2s)^{5/3}]$ , where  $E_F = (\hbar^2/2m^*)(3\pi^2 n)^{2/3}$  is the Fermi energy. Substituting this expression into Eq. (3) and expanding  $\mathcal{F}$  in  $s$  and  $m$  near the Curie temperature, we obtain  $T_C = (\Gamma_{ex}^2/k_B) N_i N_d J(J+1)/12$ , where  $N_0 = 3n/2E_F$  is the electronic density of states at  $E_F$ . This is the standard expression for  $T_C$  given, for example, as Eq. (7) of Ref. [6].

The possibility of reentrant ferromagnetism in semiconductors was first discussed over forty years ago [22], and again recently [23]. In neither case was the thermodynamic stability of the magnetism discussed. Moreover, the role of the donor electrons was not included, an omission that can lead to contradictions. For example, in Ref. [23] it was assumed that the conduction-electron density has no explicit dependence on the magnetization. This assumption is justified only if the spin-splitting of the donor level ( $\Delta_d$ ) and conduction band ( $\Delta$ ) are equal, i.e.  $\gamma = 1$ . However, the self-consistency equation given in Ref. [23] for the magnetization of the impurity spins is only correct for the case  $\gamma = 0$ . This can be seen by substituting our Eq. (8) into Eq. (9) and comparing to the corresponding equation in Ref. [23]. This internal inconsistency has substantial consequences. Specifically, for the case  $\gamma = 1$ , expanding the self-consistency equation for small magnetization in the vicinity of the critical temperature yields  $T_C = T_C^0 \nu(0, T_C)$ . But for the case  $\gamma = 0$ , a similar expansion yields the qualitatively different dependence  $T_C = T_C^0 \sqrt{\nu(0, T_C)}$ .

In its present form, our model does not include several physical effects which could alter the magnetic ordering at low temperature. (1) Hopping and Coulomb fluctuations will broaden the donor levels into an impurity band of localized states [24]. (2) The neutral donors may form bound magnetic polarons [25] by aligning nearby impurity spins, thereby increasing the donor ionization energy  $\varepsilon_d$ . (3) There could be a substantial direct antiferromagnetic interaction between nearest-neighbor impurity spins. This would have two consequences:  $\mathcal{F}$  in Eq. (3)

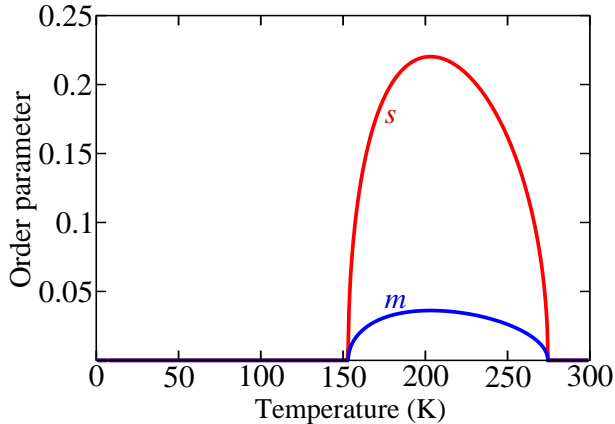


FIG. 3: Temperature dependence of order parameters  $s$  and  $m$  when percolation is omitted (see text). Materials parameters are the same as in Fig. 1, except for  $m^*=2.5$ .

would acquire a contribution  $\propto m^2$ , while the argument in the mean-field expression for  $m$  in Eq. (9) would be reduced by a term  $\propto m$ .

All three of these effects would suppress ferromagnetism at low temperatures. While the situation is fairly complex, we can describe it qualitatively by omitting the percolation term in Eq. (3), i.e. by setting  $\nu_d(s, T) = 0$  or, equivalently, by taking  $a_B \rightarrow 0$  in Eq. (7). Figure 3 shows the resulting behavior for  $s(T)$  and  $m(T)$ . The striking feature is that the ferromagnetism is absent at both low and high temperatures, corresponding to anti-ferromagnetic and paramagnetic states, respectively. A similar interpretation of reentrant ferromagnetism was proposed in Ref. [22] to explain experimental data on (Li,Mn)Se [26]. Furthermore, both of the scenarios for reentrant ferromagnetism shown in Figs. 2 and 3 are consistent with the recent experiments in (In,Mn)Se [27]. With the change in Mn-concentration there is a change in the number of peaks in the temperature dependence of dynamic magnetic susceptibility supporting the existence of either two or three distinct critical temperatures (recall Figs. 2 and 3). While, for simplicity, we have focused on the parameters for Eu-based semiconductors, there is a need to explore other FS for a possible reentrant ferromagnetism.

Predictions of reentrant ferromagnetism could be directly tested in transport experiments. For example, in conventional (non-reentrant) spin light-emitting diodes [4] the emitted light is circularly polarized if the injected carriers are spin-polarized. As the temperature is raised, there is a monotonic decrease in the degree of polarization of the electroluminescence, due to the decreased polarization of the carriers. By using a reentrant FS as the spin injector, a nonmonotonic temperature de-

pendence of the electroluminescence, similar to that for  $s(T)$  in Figs. 2 or 3, would be expected. Reentrant behavior could also be detected electrically, without a spin-LED, by demonstrating non-monotonic temperature dependence of the magnetoresistance in a semiconductor heterojunction [14, 28] that includes a reentrant FS.

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